




## Mercury free miniature zinc-air cells.

Patent number: EP0560579  
Publication date: 1993-09-15  
Inventor: MANSFIELD ROBERT NILE JR (US); SCARR  
ROBERT FRANCIS (US)  
Applicant: EVEREADY BATTERY INC (US)



Also published as:

 US5279905 (A1)  
 JP6013112 (A)  
 EP0560579 (B1)

Classification:

- international: *H01M2/02; H01M12/06; H01M2/02;*  
*H01M12/00; (IPC1-7): H01M2/02;*  
*H01M12/06*

Cited documents:

 US4500614  
 JP55119345

- european:

Application number: EP19930301783 19930309

Priority number(s): US19920848497 19920309

[View INPADOC patent family](#)

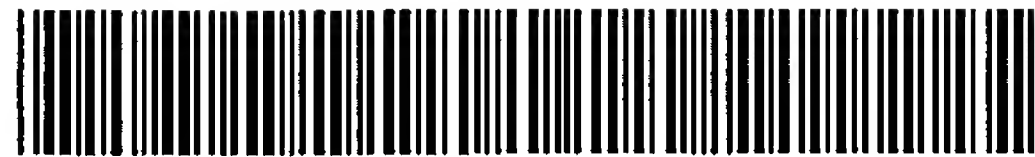
[Report a data error here](#)

### Abstract of EP0560579

The present invention provides a miniature zinc-air cell employing an anode cup (22) that has a layer (34) of a first metal deposited over at least a portion of a layer of (33) a second metal coating a surface of a conductive substrate (37), such that the layer of the first metal contacts the anodic mixture (26) of the cell, thereby enabling the anodic mixture (26) to be made with little or no mercury. A method for producing anode cups is also disclosed.

---

Data supplied from the *esp@cenet* database – Worldwide



⑪ Publication number : **0 560 579 A1**

⑫

**EUROPEAN PATENT APPLICATION**

⑳ Application number : **93301783.2**

㉑ Int. Cl.<sup>5</sup> : **H01M 2/02, H01M 12/06**

㉒ Date of filing : **09.03.93**

㉓ Priority : **09.03.92 US 848497**

㉔ Date of publication of application :  
**15.09.93 Bulletin 93/37**

㉕ Designated Contracting States :  
**BE DE DK ES FR GB**

㉖ Applicant : **EVEREADY BATTERY COMPANY,  
INC.  
Checkerboard Square  
St. Louis Missouri 63164 (US)**

㉗ Inventor : **Mansfield, Robert Nlle Jr.  
13535 South Partridge Drive  
Valley View Ohio 44125 (US)  
Inventor : Scarr, Robert Francis  
1370 Patti Park  
Westlake Ohio 44145 (US)**

㉘ Representative : **Harrison, Susan Joan et al  
Marks & Clerk 57-60 Lincoln's Inn Fields  
GB-London WC2A 3LS (GB)**

㉙ **Mercury free miniature zinc-air cells.**

㉚ The present invention provides a miniature zinc-air cell employing an anode cup (22) that has a layer (34) of a first metal deposited over at least a portion of a layer of (33) a second metal coating a surface of a conductive substrate (37), such that the layer of the first metal contacts the anodic mixture (26) of the cell, thereby enabling the anodic mixture (26) to be made with little or no mercury. A method for producing anode cups is also disclosed.

The present invention relates to a miniature zinc-air cell containing no or substantially no mercury and including an anode cup which is coated and which contacts the zinc electrode of the cell. The present invention also provides a process for the manufacture of such a coated anode cup for use in a miniature zinc-air cell containing no or substantially no mercury.

Alkaline electrochemical cells employing a zinc anode and an alkaline electrolyte have become commercially important as a relatively high rate source of electrical energy. The alkaline electrolyte, which is usually concentrated aqueous potassium hydroxide, is a principal factor contributing to the ability of these cells to deliver high rates of electrical energy. Such cells are clearly superior when compared with the older Leclanche cells having an electrolyte of zinc chloride and/or ammonium chloride.

However, the presence of alkali in an electrochemical cell has both advantages and disadvantages. The disadvantages include, for instance, the strong promotion by the alkali of the reaction of water with zinc, thereby causing corrosion. Without means to control this reaction, and therefore the corrosion, the shelf life of alkaline zinc cells would be unacceptably short. A further disadvantage is the release of hydrogen gas by the reaction between alkali and zinc. As a result of this, there may be a danger of electrolyte leakage and/or cell disassembly.

In commercial alkaline zinc cells, the reaction between zinc and alkali has been controlled or reduced to an acceptable rate by the addition of mercury to the cell. However, it has recently become apparent that the introduction of mercury into the environment may be a hazard to human health, as well as to other forms of life. While individual cells contain only a small amount of mercury, the very large number of zinc alkaline cells marketed today could cause significant quantities of mercury to enter the environment upon disposal of the cells.

Because of the heightened consciousness towards the environment, many attempts have been made to reduce the amount of mercury used in an alkaline cell, and even to eliminate the mercury component altogether.

In alkaline batteries of the most common and standard sizes, e.g. the AA, C and D sizes, this mercury reduction has taken many forms. For example, in US-A-3,847,699 an alkaline zinc-manganese dioxide cell is described in which the proportion of mercury needed to achieve acceptable storage life can be reduced by the addition of small amounts of an ethylene oxide polymer. US-A-4,500,614, on the other hand, tackles the problem of reducing the amount of mercury in a standard alkaline cell by amalgamating an alloy powder made of zinc and at least two of the metals gallium, indium and thallium to form the anode. The effect of this is to prevent corrosion of the zinc by the alkaline electrolyte, and thereby the generation of hydrogen gas and subsequent leakage of the electrolyte.

Also relevant is Japanese unexamined patent application 01-307161, which is directed to a mercury-free standard alkaline cell wherein the collector for the negative electrode is coated with indium and/or lead. The coating can be applied by any appropriate method, including electroplating.

Alternative methods to reduce the corrosion of the zinc electrode are described in DE-B-1,086,309 and JP-A-1958-3204. German Patent 1,086,309 discloses an alkaline zinc cell in which an indium compound is added to the electrolyte and/or indium metal is alloyed with refined zinc so as to protect the zinc against corrosion in an acidic, neutral or alkaline electrolyte. Japanese Publication No. 1958-3204, published April 26, 1958, on the other hand, states that the addition of 0.0001% to 2.0% indium to pure zinc base alloy containing one, two, or more of the metallic elements Fe, Cd, Cr, Pb, Ca, Hg, Bi, Sb, Al, Ag, Mg, Si, Ni, Mn, etc., results in the formation of a zinc alloy which has a high corrosion resistance and which is suitable for use in primary cells.

As the large amount of prior art indicates, manufacturers of alkaline batteries have invested substantial amounts of time and money in the effort to develop mercury-free batteries. The first batteries to incorporate mercury-free constructions were the AA, C and D standard alkaline batteries. These batteries have historically used the largest quantities of mercury per cell and are the most common sizes and type purchased by consumers. Therefore, removing mercury from these batteries has proved to be the best way to make significant reductions to the quantity of mercury currently entering the general waste stream by disposal of used alkaline cells.

However, in addition to developing mercury-free standard alkaline batteries, the development of miniature zinc-air cell constructions which are free of mercury has also proved desirable. Miniature zinc-air cells include those which are smaller than the standard size battery, for example the "675 size" which measures 5.33 mm in height and 11.557 mm in diameter. While a layman may believe that the technology used to produce mercury-free standard alkaline batteries can be used to produce mercury-free miniature zinc-air batteries, this is not, in fact, the case. Instead, the manufacturers of miniature zinc-air batteries have found that additional technology is needed before mercury-free miniature zinc-air cells can be manufactured on a commercial basis. Because the construction of a miniature zinc-air battery is substantially different from the construction of a stan-

standard alkaline battery, new processes and techniques that are only relevant to the miniature zinc-air cells are required.

In view of the above, it is apparent that further development in the field of mercury free miniature zinc-air cells is required.

5 It is an object of the present invention to provide a miniature zinc-air cell which has a reduced amount of mercury of less than 6%, preferably less than 3%, in the zinc-containing electrode and most preferably having a mercury-free zinc-containing electrode.

10 It is another object of the present invention to provide a miniature zinc-air cell with a zinc-containing electrode that is substantially free or completely free of mercury and wherein the surface of the electrode cup contacting the zinc-containing electrode is treated so as to compensate for the absence of mercury in the cell.

It is a further object of the present invention to provide a method for producing a treated electrode cup for use in a miniature zinc-air cell containing no, or very little, mercury.

These and other objects of the invention will be apparent from the following description.

15 The present invention provides, in a first aspect, an alkaline miniature zinc-air cell including a zinc-containing anode, containing no, or substantially no, mercury, and an anode cup, the cup physically and electrically contacting the anode and consisting of a conductive substrate, characterised in that a surface of the cup contacting the anode is at least partially coated with copper, or an alloy containing copper, to form an underlayer, at least a portion of the underlayer being overlaid with a layer of indium, or an alloy containing indium.

20 In an embodiment of this aspect of the invention, the surface of the anode cup opposing that surface contacting the anode is coated with a layer of nickel.

In a second aspect, the present invention provides a method for the production of an anode cup for an alkaline miniature zinc-air cell as hereinabove defined.

25 In a further aspect, the present invention provides a zinc-air cell employing a manganese dioxide-containing electrode and a zinc-containing electrode assembled within a conductive housing comprising a cathode cup having at least one opening to permit air to enter and said cathode cup being electrically contacted to the manganese dioxide containing electrode; an anode cup electrically and physically contacted to the zinc-containing electrode; said cathode cup secured to and insulated from the anode cup; and said anode cup comprising a conductive substrate having on a portion of at least the inner surface contacted to the zinc-containing electrode an underlayer of copper and a top layer of indium.

30 In the present invention, the surface of the anode cup contacting the anode has at least a partial coating of copper or an alloy containing copper. The effect of this underlayer is to resist passivation and/or attack by the electrolyte in the cell, characteristics which the conductive substrate of the anode cup may or may not possess. The underlayer also provides a surface onto which the overlayer can be effectively applied.

35 In the cell of the present invention, when the underlayer is formed from an alloy containing copper, this alloy should not contain an element that could be replaced by indium. It is most preferred, however, that the coating is formed from substantially pure copper.

40 The thickness of the underlayer is not essential to the present invention and a thickness appropriate to the application of the cell can readily be determined by the man skilled in the art. We generally prefer that the underlayer is more than  $0.0254\text{ }\mu\text{m}$  [1 microinch] thick, more preferably more than  $2.54\text{ }\mu\text{m}$  [100 microinches] thick. It is most preferred that this layer is from  $25.4\text{ }\mu\text{m}$  [1000 microinches] to  $50.8\text{ }\mu\text{m}$  [2000 microinches] thick.

The underlayer on the anode cup of the cell according to the present invention is at least partially coated with the metal indium, or an alloy containing indium. It is most preferred that the coating is formed from pure indium.

45 The metal coating on the anode cup may be continuous or discontinuous. The choice of continuity or discontinuity of the coating is dependent on, for example, the environment in which the cell is to be used. Thus for example, when the environment involves high temperatures, it may be advantageous for the coating to be discontinuous, i.e. to cover only a part of the surface of the anode cup contacting the anode. In such situations it is preferred that the coating covers less than 95% of the surface area of the anode cup contacting the anode.  
50 The presence of a discontinuous coating, as described above, will allow a portion of said underlayer to contact the zinc-containing electrode. For use of the cell in ambient temperatures, for example of about  $20^{\circ}\text{C}$ , however, a continuous coating is preferred.

55 The thickness of the metal coating on the anode cup is dependent on various factors, including, for example, the requirement for elimination of mercury from the cell without affecting the characteristics of the cell; and the cost of the metal layer. Although the upper limit of the thickness of the metal layer is largely determined by cost, we prefer that this thickness does not exceed  $1.27\text{ }\mu\text{m}$  [50 microinches]. A suitable range of thickness for this layer is  $0.0127\text{ }\mu\text{m}$  [0.5 microinches] to  $1.27\text{ }\mu\text{m}$  (50 microinches] although, in practical terms, no additional benefit is achieved if the thickness of the layer exceeds  $0.762\text{ }\mu\text{m}$  (30 microinches]. It is generally pre-



ferred to keep the thickness within the range 0.0254  $\mu\text{m}$  [1 microinch] to 0.127  $\mu\text{m}$  [5 microinches] and most preferably within the range 0.0254  $\mu\text{m}$  [1 microinch] to 0.0762  $\mu\text{m}$  [3 microinches].

The anode cup of the present invention is formed from a conductive substrate. Typically, this substrate is a metal, and it is preferred that this substrate is cold rolled steel, stainless steel or brass. Because cold rolled steel is a satisfactory substrate and is inexpensive, it is the preferred substrate for the anode cup. The steel may be obtained in the form of rolls of strip stock in which the width of the strip is much greater than the thickness of the material. This means that the material has two broad surfaces (i.e. faces) and two edge surfaces. It is preferred that the cross-section of the strip is flat, as opposed to concave or convex.

Anode cups used by many manufacturers of miniature zinc-air cells are made from strip stock, as described above, comprising two or more metal layers laminated together. Such a laminated strip generally comprises a relatively thick component which serves as the conductive substrate, this thick component usually being steel. The laminate is then formed by deposition of thinner coatings of a conductive metal, such as copper, or an alloy containing copper, onto the surface of the thick steel component. In the present invention the conductive substrate may be a single layer, e.g. of steel, or it may be a laminate, for example of two or three layers, one of the layers being steel and another being, for example, copper.

In a further embodiment of the present invention, the surface of the anode cup opposing that contacting the anode, i.e. the surface directed towards outwards from the cell, may be coated, for example to prevent rusting of the surface of the conductive substrate which would otherwise be exposed to moisture in the air. Suitable coating materials include, for example, nickel. Nickel is the most preferred because of its bright appearance and its resistance to corrosion.

The zinc-air cells of the present invention comprise a zinc-containing electrode. Such electrodes are commonly used in cells of this type, and the construction of such electrodes is not essential to the present invention. The zinc-containing electrode of this invention does, however, contain no, or substantially no, mercury. The absence of mercury in this electrode is compensated for by the metal coating on the anode cup. It is preferred that the zinc-containing electrode contains less than 6 % mercury, and it is more preferred that this amount of mercury is less than 3 %. Most preferred are zinc-containing anodes which contain no mercury.

The present invention also provides a process for the manufacture of an anode cup suitable for use in a mercury free alkaline miniature zinc-air cell. This process comprises the steps of deposition of a layer of copper or an alloy containing copper, to form an underlayer, onto the surface of a conductive substrate, application by electroplating of indium, or an alloy containing indium, onto at least a portion of the underlayer, and forming the coated material into a cup shaped body, such that the coated portion is on the inside of the cup shaped body.

The preferred process for manufacturing an anode cup suitable for use in a cell according to the present invention is to plate one side of a steel strip, for example strip stock, as hereinabove described, with an underlayer material, such as copper. In a further step, the opposite side of the steel strip, i.e. that side not coated with copper, is plated with an outer layer, for example nickel. Finally, a metal, such as indium, is deposited onto as much of the copper layer as is required, thereby forming a multilayer strip. Discs, from which the anode cups are formed, are punched from the multilayer strip and are processed through conventional metal forming equipment to produce the anode cup. The processing must take place such that the indium layer forms the concave portion, or inner surface, of the cup, and the nickel coating forms the convex portion, or outer surface, of the cup.

Electroplating of the metal onto the surface of the conductive substrate offers several advantages when compared to other methods for depositing a metal onto the surface of the current collector of an alkaline cell. These advantages are listed below.

1. Electrodeposition of the metal, for example indium, onto the conductive substrate, for example strip stock, means that the uniformity of the metal plating can be accurately controlled. Clearly, the uniform deposition of a metal onto the surface of a pre-formed anode cup would present extreme difficulties, due to the cup configuration of this cell component.

2. Electroplating directly onto a conductive material in the form of strip stock enables the manufacturer to control with accuracy the location of the plated metal. Selective control of the plating process is of importance to the manufacturers of batteries. Alternative methods of plating, for example barrel plating, would not be appropriate in this instance. Pre-formed cups coated via barrel plating would be coated on both sides of the conductive substrate, due to the requirements of a barrel plating method. As discussed above, it is important that the metal coated onto the surface of the anode cup which contacts the anode does not also contaminate the opposing surface of the anode cup, i.e. that surface which is directed away from the cell.

3. Using an electroplating method, it is possible to control the thickness of metal applied to the substrate with greater accuracy. Thus, the preferred thickness of the metal, as discussed above, can be readily ob-

tained using an electrodeposition process. Use of other, conventional plating techniques, such as the reliance upon metal ions in the electrolyte to plate onto the surface of the anode cup, does not allow for the accurate deposition of the quantities of metal required by the present invention onto the surface of the anode cup.

4. In specific applications a discontinuous layer of metal coating is preferred. Use of an electroplating technique allows for the accurate deposition of the metal onto the surface of the anode cup, and thereby allows for the deposition of a discontinuous layer. This is particularly the case when there is an underlayer on the anode cup, such as a copper underlayer, and it is important that portions of this underlayer can contact the anode directly, so as to ensure that the impedance of the cell does not increase excessively when the cell is stored at high temperatures.

5. Yet a further advantage of the present invention is that the electrodeposition technique is effective when chemical displacement of metal ions, such as indium ions, cannot be used. The chemical displacement process relies upon the presence of a reducing component, such as zinc, on the surface of the substrate. If the surface of the conductive substrate does not contain the reducing component, the metal, e.g. indium, cannot be deposited by chemical deposition.

The alkaline miniature zinc-air cell of the present invention may then be formed by inserting a zinc-containing gel into the cavity defined by an anode cup, formed as hereinabove described, and then combining the filled anode cup with a cathode cup containing a metal oxide, for example manganese dioxide, this cup having at least one opening in order to permit air to enter the cell. A completed electrochemical cell results after the addition of a gasket, which gasket, typically made from plastic, such as nylon, so as to be electrically non-conductive, electrically separates the anode cup from the cathode cup and prevents leakage of the electrolyte from the cell.

The present invention will now be further illustrated with reference to the accompanying drawing which shows, in cross-section, a miniature zinc-air cell employing an anode cup in accordance with the present invention.

As shown in the drawing, the largest component of the zinc-air cell is an open ended metal container 2, identified as a cathode cup. The cathode cup 2 is generally made from nickel plated steel that has been formed so that it has a relatively flat central region 4 which is continuous with and surrounded by an upstanding wall 6 of uniform height. Two small holes 8 are punched into the bottom 4 of the cup 2 to act as air-entry ports. A layer of porous material 10 covers the interior surface of the air holes and acts as an air distribution membrane. A layer of polytetrafluoroethylene 12 covers the whole of the bottom of the cathode cup 2, including the air distribution membrane 10.

The second major component of the cell is an air electrode 14 which is positioned adjacent the inside surface of the polytetrafluoroethylene layer 12. This electrode 14 contains several components, including: a metal screen 16; a mixture of manganese oxides and carbon embedded in the screen 16; a barrier film 18 which prevents the anode's electrolyte from moving into the cathode 14; and a soakup separator 20.

The third component of the cell is a generally cup-shaped metal component 22 which forms the top of the cell and is generally referred to as the anode cup. In the figure, the edge 24 of the anode cup has been rolled backward upon itself thereby creating a double wall. The anode cup 22 can be made from a trilaminate material comprising copper 33 that has been laminated to the bare side of a nickel-clad steel strip. A nickel layer 35 protects the exterior surface of steel strip 37, which is located between nickel layer 35 and copper layer 33. Other laminated materials from which the anode cup may be made include a bilaminate, for example copper on a stainless steel substrate, or a laminate made from more than three layers. Round disks punched from this laminated metal strip are then formed into anode cups. In this figure, the copper layer 33 forms the inside surface of the anode cup and directly contacts the anodic mixture.

The fourth component of the cell is the anodic mixture 26, which can comprise a mixture of zinc particles, electrolyte and organic compounds, such as binders and corrosion inhibitors, which make up the battery's anode. A tubular shaped ring or gasket 28, made from an elastomeric material, serves as the seal. The bottom edge of the gasket 28 has been formed to create an inwardly facing lip 30 which abuts the rim of the anode cup 22. The cathode cup 2, along with the inserted air electrode 14 and associated membranes, are inverted and pressed against the anode cup/gasket assembly, which are preassembled. While inverted, the edge of the cathode cup 2 is colleted inward. The rim 32 of the cathode cup is then compressed against the elastomeric gasket 28 between the cathode cup 2 and the anode cup 22, thereby forming a seal and an electrical barrier between the anode cup 22 and the cathode cup 2. A suitable tape 38 can be placed over the opening 8 until the cell is ready for use.

In accordance with the present invention, a layer of indium 34 (shown exaggerated) is deposited on one side of the anode disc before it is formed into a cup 22. As shown in the drawing, the indium layer 34 forms the inner surface of cup 22 defining a cavity 36 into which the anodic mixture 26 is fed. As stated above, the

indium layer may be a continuous layer or a discontinuous layer. Since the underlayer of the interior surface of the cup 22 in this embodiment is copper 33, the chemical displacement process used in the art can not be used since this process relies on the presence of zinc or some other reducing component.

The following examples illustrate the advantages of the cells of the present invention and are not intended to limit the scope of the invention in any way.

#### EXAMPLE 1

Several batches of miniature zinc-air cells were assembled in order to evaluate the impact of electroplating indium on to the surface of the anode cup that contacts the anode. All cells measured approximately 11.557 mm [0.455 inch] in diameter by 5.33 mm [0.210 inch] in height. These batteries are commonly referred to as "675 size".

In the first of two tests, the control batch, designated Batch A, contained 6 % mercury (mercury/zinc ratio) in the anode, and the anode cup was not plated with indium. Batch B had no mercury in the anode and no indium plated onto the anode cup. Batches C to G had no mercury in the anode, but the anode cups were plated with the following thicknesses of indium:

Batch C, 0.0254  $\mu\text{m}$  [one microinch];

Batch D, 0.0762  $\mu\text{m}$  [three microinches];

Batch E, 0.381  $\mu\text{m}$  [fifteen microinches];

Batch F, 0.762  $\mu\text{m}$  [thirty microinches]; and

Batch G, 1.27  $\mu\text{m}$  [fifty microinches].

Each Batch was separated into four sublots consisting of three cells each. All cells were then discharged continuously across a 625 ohm resistor to 0.9 volts. The test conditions for the cells varied as follows.

A. The first subplot was tested within a few days after the cells had been assembled. The second subplot was aged for one week at 71°C and then tested. The third subplot was aged for twenty days at 60°C prior to testing. The fourth subplot was aged for forty days at 60°C and then tested.

The charge for each subplot (measured in milliamphours) to the designated cutoff is shown in Table 1. These data support the unexpected conclusion that, when comparing the first three sublots, all cells in Batches C to G, i.e. those with indium plated anode cups but no mercury in the anode, provided more service than comparably aged cells in Batch A (6% mercury and no indium) or Batch B (no mercury and no indium).

A clear conclusion cannot be drawn from the cells which were aged for forty days at 60°C (i.e. the fourth subplot in each case) because the cells from two of the five indium plated batches provided better service than the control, while the cells from two other batches provided slightly less service and those from one batch had significantly less service. These inconsistent results are not unusual for cells tested at the relatively high temperature of 60°C for forty days, because some factor other than the collector-/anode interface controls cell behaviour under these conditions.

Table I

5		A	B	C	D	E	F	G
		6% Hg/Zn	Zero Hg indium plating thickness					
10	Sub lot	(non- plated)	(non- plated)	0.0254 $\mu$ m	0.0762 $\mu$ m	0.331 $\mu$ m	0.762 $\mu$ m	1.27 $\mu$ m
	1	initial	494	477	533	533	520	516
15	2	1 wk at 71°C	494	461	532	533	511	517
	3	20 days at 60°C	496	443	500	491	511	502
20	4	40 days at 60°C	491	461	504	487	480	504
								423

25 B. Five cells from each of the batches and sublots were impedance tested after storage at 71°C. These data are shown in Table II. These data support the unexpected conclusion that mercury-free miniature alkaline zinc-air cells which contain indium-electroplated anode cups did provide significantly lower impedance values when compared to similarly aged cells containing no mercury and no indium, and comparable impedance when compared to cells containing six percent mercury and no indium.



Table II

	A	B	C	D	E	F	G
	6%	Zero Hg					
	Hg/Zn	indium plating thickness					
	(non-plated)	(non-plated)	0.0254 $\mu\text{m}$	0.0762 $\mu\text{m}$	0.381 $\mu\text{m}$	1.27 $\mu\text{m}$	1.27 $\mu\text{m}$
initial	6.3	7.5	6.9	7.7	5.4	5.6	5.3
2 weeks	8.0	20.2	6.6	7.4	8.1	8.4	5.3
4 weeks	8.9	35.0	9.8	9.7	9.5	10.3	3.8
6 weeks	8.4	73.0	10.4	10.0	10.3	11.7	11.7
8 weeks	9.0	*	10.2	11.4	12.7	14.1	13.1

\* Test stopped due to cell leakage.

## EXAMPLE 2

Several batches of miniature zinc-air cells were assembled in order to evaluate the impact of electroplating indium onto the surface of the anode cup contacting the anode. These cups were then incorporated into cells which also contained 0.2 mg of indium in the anode mass per gram of zinc. The indium was added to the zinc as indium hydroxide.

As in Example 1, all batteries in this test measured approximately 11.557 mm [0.455 inch] in diameter by 5.33 mm [0.210 inch] in height. The composition of the anode cup in the control batch in this Example, designated Batch A, was identical to that in the control Batch in Example 1. The cells in this batch did not have indium hydroxide added to the anode. Batch H contained no mercury, no indium plated on the anode cup and 0.2 mg of indium in the anode mass per gram of zinc. Batches I and J were identical to Batch H except that their anode cups were electroplated with indium approximately 0.0254  $\mu\text{m}$  [one microinch] thick and 0.0762  $\mu\text{m}$  [three microinches] thick, respectively.

Each batch was separated into four sublots consisting of three cells each. All cells were then discharged continuously across a 625 ohm resistor to 0.9 volts. The test conditions for the cells varied as follows.

A. The first subplot was tested within a few days after the cells had been assembled. The second, third and fourth sublots were aged prior to testing for one week at 71°C; twenty days at 60°C and forty days at 60°C, respectively. The charge for each subplot (measured in milliamphours) to the designated cutoff is shown in Table III. The data support the conclusion that all cells in the first three sublots of Batches I and J, i.e. those with indium plated anode cups and no mercury in the anode, provided more service than comparably aged cells in Batch A or Batch H. A clear conclusion cannot be drawn from the cells which were aged for forty days at 60°C, i.e. the fourth subplot in each case, because, in these sublots, the cells from Batch I provided less service than the cells from Batch A, while the cells from Batch J provided more service than the cells from Batch A. As was explained earlier, this type of anomaly in service data is not unusual when cells are stored for a relatively long time (i.e. forty days) at a relatively high temperature 60°C).

Table III

		A	I	J	H
		6 % Hg/Zn	<u>Indium Plating</u> <u>Thickness</u>		Zero Hg
<u>Sub Lot</u>	<u>Cell Age</u>	<u>(non-plated)</u>	<u>0.0254 <math>\mu</math>m*</u>	<u>0.0761 <math>\mu</math>m*</u>	<u>(non-plated)*</u>
1	Initial	494	514	544	507
2	1 wk at 71°C	494	515	526	480
3	20 Days at 60°C	496	510	510	483
4	40 Days at 60°C	491	485	523	455

\* 0.2 mg indium/gm zinc added as indium  
hydroxide

B. Five cells from each of the batches and sublots having the compositions shown above were impedance tested after storage at 71°C. The results are shown in Table IV (charge is measured in milliamphours).

These data support the conclusion that mercury-free miniature alkaline zinc-air cells which contained indium hydroxide in the anode and indium-electroplated anode cups did provide lower impedance values when compared to both similarly aged cells containing no mercury, no indium electroplated onto the anode cup, but indium hydroxide in the anode, or cells containing six percent mercury and no indium at all.

Table IV

	A	I	J	H
	6% Hg/Zn	<u>Indium Plating</u> <u>Thickness</u>		Zero Hg
<u>Cell Age</u>	<u>(non-plated)</u>	<u>0.0254 <math>\mu\text{m}</math>*</u>	<u>0.0762 <math>\mu\text{m}</math></u>	<u>(non-plated)</u>
<b>Initial</b>	6.3	8.0	6.7	7.4
<b>2 weeks</b>	8.0	7.1	7.3	10.6
<b>4 weeks</b>	8.9	7.6	8.3	11.6
<b>6 weeks</b>	8.4	7.4	8.5	16.5
<b>8 weeks</b>	9.0	7.9	8.9	19.9

The following conclusions can be deduced by comparing the service and impedance data in Example 1 and Example 2.

(a) The addition of 0.2 mg of indium per gram of zinc to the anode mass of mercury-free miniature alkaline zinc-air cells which contain indium-electroplated anode cups did not significantly improve or detract from service performance on a 625 ohm continuous test.

(b) The addition of 0.2 mg of indium per gram of zinc to the anode mass of mercury-free miniature alkaline zinc-air cells which contain indium-electroplated anode cups did improve the impedance of cells stored at 71°C.

### Claims

1. An alkaline miniature zinc-air cell including a zinc-containing anode (26), containing no, or substantially no, mercury, and an anode cup (22), the cup physically and electrically contacting the anode and consisting of a conductive substrate (37), characterised in that a surface of the cup contacting the anode is at least partially coated to form an underlayer with copper or an alloy containing copper (33), at least a portion of said underlayer being overlaid with indium (34), or an alloy containing indium.
2. A cell according to claim 1 in which the indium or an alloy containing indium, coating (34) is from 0.0127  $\mu\text{m}$  to 1.27  $\mu\text{m}$  thick.
3. A cell according to claim 1 in which the indium or alloy containing indium, coating (34) is from 0.0254  $\mu\text{m}$  to 0.0762  $\mu\text{m}$  thick.
4. A cell according to any one of claims 1 to 3 in which the indium, or alloy containing indium, coating (34) is discontinuous.
5. A cell according to any one of claims 1 to 4 in which the metal of the coating (34) is pure indium.
6. A cell according to claim 5, in which the metal of the underlayer (33) is pure copper.
7. A cell according to claim 6, in which the underlayer (33) is more than 0.0254  $\mu\text{m}$  thick, preferably more than 2.54  $\mu\text{m}$  thick.

8. A cell according to claim 7 in which the underlayer (33) is from 25.4  $\mu\text{m}$  to 50.8  $\mu\text{m}$  thick.
9. A cell according to any preceding claim in which the underlayer (33) is substantially totally overlaid with indium (34), or an alloy containing indium.
- 5 10. A cell according to any preceding claim in which the surface of the anode cup (22) opposing that contacting the anode is coated with a layer of nickel.
11. A cell according to any preceding claim in which the conductive substrate (37) is steel or brass.
- 10 12. A cell according to claim 11 in which the conductive substrate (37) is cold rolled steel.
13. A cell according to any preceding claim in which the zinc-containing electrode (26) contains less than 6 % by weight of mercury.
- 15 14. A cell according to claim 13 in which the zinc-containing electrode (26) contains less than 3 % by weight of mercury.
15. A cell according to claim 13 in which the zinc-containing electrode (26) contains no mercury.
- 20 16. A cell according to any preceding claim in which the zinc-containing electrode (26) contains a small amount of indium.
17. A process for the manufacture of an anode cup (22) suitable for use in a cell as defined in claim 1, which process comprises deposition of a layer of copper or an alloy containing copper, to form an underlayer (33), onto one surface of a conductive substrate (37), application by electroplating of indium (34), or an alloy containing indium, onto at least a portion of said underlayer (33), and forming the coated material into a cup-shaped body, such that the coated portion is on the inside of the cup-shaped body.
- 25 18. A process according to claim 17 in which the conductive substrate (37) is a steel strip.
- 30 19. A process according to claim 18 in which the conductive substrate (37) comprises a laminate of two or more layers.
20. A process according to claim 19 in which the conductive substrate (37) comprises a steel strip which is coated on one surface with a layer of nickel.
- 35 21. A process according to claim 19 which comprises plating one side of a steel strip (37) with copper, plating the other side of the steel strip with nickel, and then electroplating indium onto the copper layer.
22. A process according to any one of claims 17 to 21 in which the indium or alloy containing indium, is applied by electrodeposition.
- 40 23. A zinc-air cell employing a manganese dioxide-containing electrode (14) and a zinc-containing electrode (26) assembled within a conductive housing comprising a cathode cup (2) having at least one opening (8) to permit air to enter and said cathode cup (2) being electrically contacted to the manganese dioxide containing electrode (14); an anode cup (22) electrically and physically contacted to the zinc-containing electrode (26); said cathode cup (2) secured to and insulated from the anode cup (22); and said anode cup (22) comprising a conductive substrate (37) having on a portion of at least the inner surface contacted to the zinc-containing electrode (26) an underlayer (33) of copper and a top layer (34) of indium.
- 45
- 50
- 55





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 93 30 1783

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	US-A-4 500 614 (A. NAGAMINE ET AL.) 19 February 1985 * claims 1-3 *	1-23	H01M2/02 H01M12/06
A	<p>---</p> <p>PATENT ABSTRACTS OF JAPAN vol. 4, no. 170 (E-35)(652) 22 November 1980 &amp; JP-A-55 119 345 ( CITIZEN TOKEI K.K. ) 13 September 1980 * abstract *</p> <p>-----</p>	1-23	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			H01M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02 JULY 1993	Examiner BATTISTIG M.L.A.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 01.92 (P0001)